UNIVERSITEIT GENT

FACULTY OF **ENGINEERING AND ARCHITECTURE**

An experimental and theoretical study of cyclopentadiene-ethene co-pyrolysis: Growth of polycyclic aromatic hydrocarbons

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Introduction

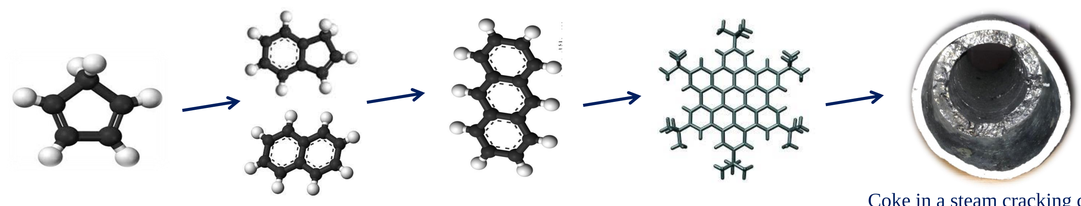
• Polycyclic aromatic hydrocarbons **(PAHs)** are a group of more than 100 chemicals that can be produced from various anthropogenic sources, such as the incomplete combustion of heating fuels, oil refining processes and the combustion of diesel fuels

•Many **PAHs** are known to be **carcinogenic** or **mutagenic** and important precursors to **soot**, which has been linked to **human morbidity** and **global warming**

• Among many potential soot precursors' reactions those involving the cyclopentadiene (**CPD**) and its corresponding cyclopentadienyl (**CPDyl**) radical are considered to be one of the most important contributors to **PAHs** and **soot formation**

Role of CPD and CPDyl

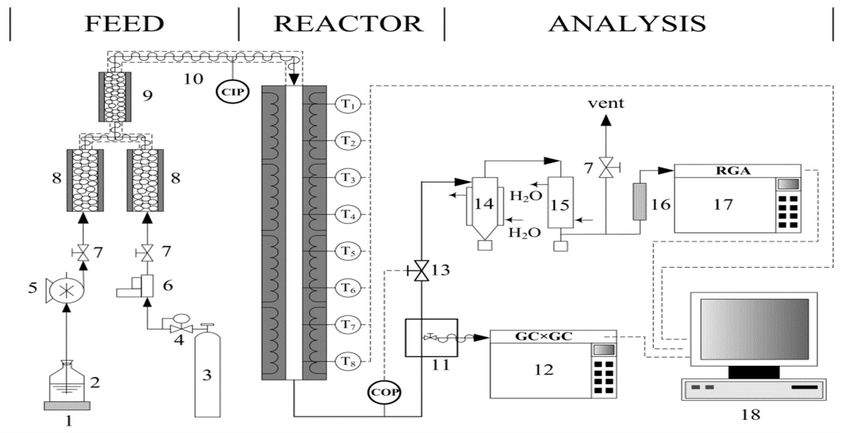
- The **CPDyl** radical is a resonance-stabilized, ambident, i.e. containing multiple reactive centers, radical that may undergo self-recombination reactions
- Due to its importance significant amount of experimental and theoretical data has been published on the gas phase chemistry involving **CPDyl** and **CPD** in the growth of **PAHs**
- This work deals both **experimentally** and **theoretically** with the growth of **PAHs** starting from **CPD** and **CPDyl**



Growth of coke deposits from smaller molecules

Coke in a steam cracking coil

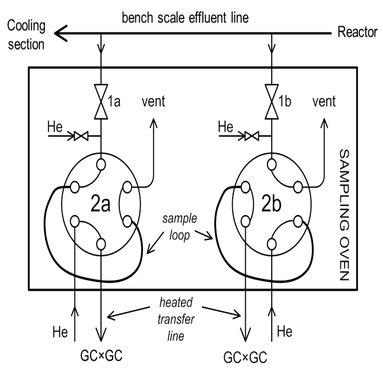
Bench scale set-up for (steam) pyrolysis



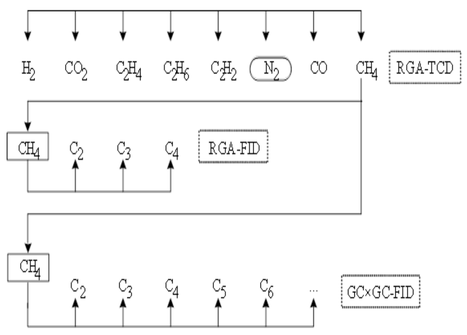
Schematic diagram of the experimental set-up indicating process gas temperatures (**Ti**) and pressure measurements (**CIP** & **COP**) (**1**-electronic balance; **2**-liquid feed reservoir (**DCPD**); **3**-gaseous diluent/internal standard (**nitrogen/ethene**); **4**-pressure reducing valve; **5**-coriolis flow meter controlled pump; **6**-coriolis mass flow controller; **7**-valve; **8**-evaporator/heater; **9**-mixer; **10**-heater; **11**-heated sampling oven; **12**-GC×GC-FID/TOF-MS for C5+; **13**-outlet pressure restriction valve; **14**-cyclone separator; **15**-condenser; **16**-dehydrator; **17**-Refinery Gas Analyzer (RGA) for C4-; **18**-data acquisition system)

•Djokic et al. *Combust. Flame*. 2014

11:On-line effluent sampling



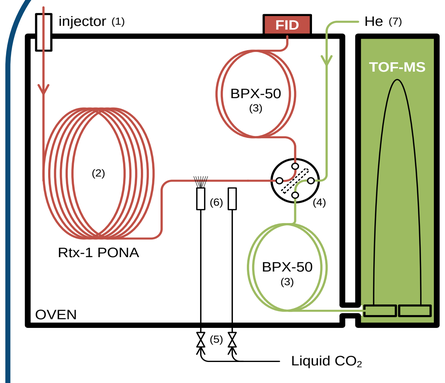
Use of reference components in the product analysis section (RGA, GC×GC)



Experimental conditions:

- Co-pyrolysis of **CPD-ethene** mixture
  - ✓ A tubular continuous flow reactor (Incoloy 800HT; 1.5 m L.; 6 mm I.D.)
  - ✓ $T_{reactor}$= 873 - 1163 K, nearly **isothermal**, COP=1.7 bara,
- Nitrogen was used as a diluent and primary **Internal standard**
  - ✓ **Dilution** of 1 mol CPD/ 1 mol C_2H_4/ 10 mol N_2, $F_{0,\,CPD}$=13.6 mg/s
  - ✓ **Argon** was used as additional (as a double-check) internal standard
- On-line sampling of the effluent using **heated transfer lines (573 K)**
  - ✓ Dedicated analysis section: **GC×GC-FID/TOF-MS + RGA(FID, TCD)**

GC×GC-FID/TOF-MS



FID
Quantitative results

TOF-MS
Peak identification

↓

Identification and quantification of ~100 compounds

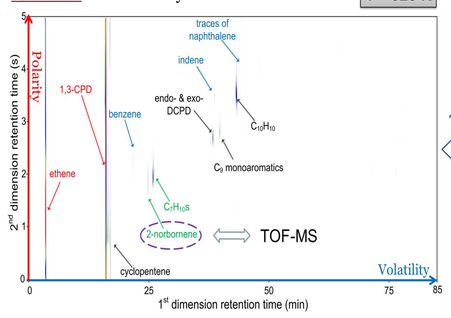
TOF-MS	
Sampling rate	**30 Hz**
EI	**70 eV**
T_{source}	**473 K**

- Thermo Scientific TRACE **GC×GC** (FID)
- Thermo Scientific Tempus **TOF-MS**

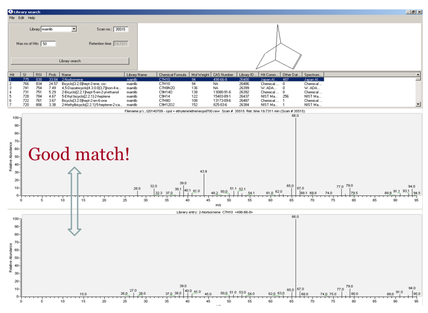
•Van Geem, Pyl, et al. *J. Chromatogr. A*. 2010

Experimental and Kinetic Modeling Results

ONLINE effluent analysis **T = 923 K**

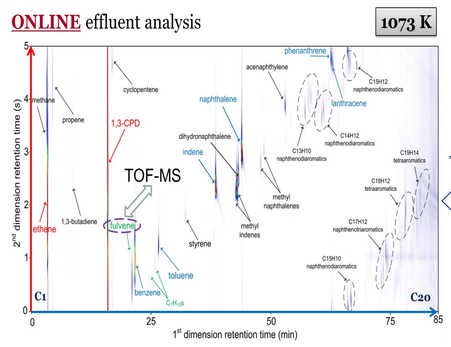


2-norbornene

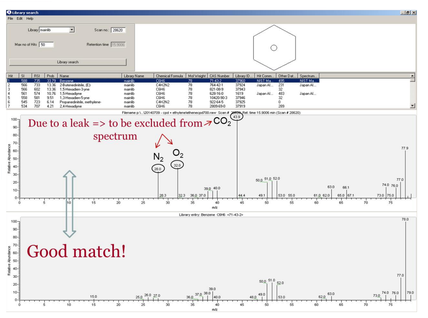


- A **very complex** product spectrum strongly depending on the temperature
- At **923 K** only limited number of pyrolysis products can be detected such as **C_7H_{10} species**, **norbornene, indene, naphthalene, benzene** and **cyclopentene**

ONLINE effluent analysis **1073 K**



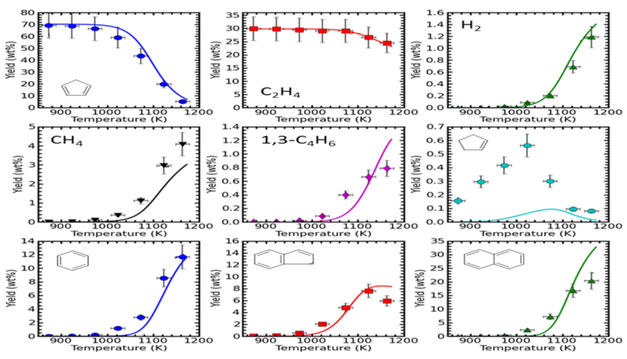
fulvene



- At **1073 K** the reactor effluent is significantly more complex, containing on the order of up to **hundred different compounds** at the highest temperature
- At the most severe conditions, **92%** of **CPD** is converted yielding almost **44 wt%** of **PAHs** with a carbon number up to **C_{20}**

Summary of the measured product yields at the reactor outlet

Conditions							
Temperature (K)	873	923	973	1023	1073	1123	1163
CPD flow rate (g/h)	49	49	49	49	49	49	49
Ethene flow rate (g/h)	21	21	21	21	21	21	21
N_2 flow rate (g/h)	206	206	206	206	206	206	206
CPD Conversion (%)	1.2	1.8	5.0	15.6	37.8	71.6	92.4
Yield (wt%)							
Permanent gases							
H_2	0.00	0.01	0.02	0.09	0.20	0.69	1.19
CH_4	0.00	0.02	0.11	0.36	1.13	2.97	4.09
Alkenes							
Ethene	29.92	29.81	29.50	29.08	29.14	26.61	24.50
Cyclopentadiene	69.16	68.76	66.47	59.09	43.57	19.88	5.35
Aromatics							
Benzene	0.01	0.03	0.21	1.16	2.77	8.56	11.68
Toluene	0.02	0.00	0.03	0.18	0.43	1.98	3.74
Styrene	0.00	0.00	0.01	0.00	0.17	0.92	2.43
Indene	0.03	0.08	0.56	2.03	4.82	7.63	5.95
Naphthalene	0.05	0.09	0.40	2.33	7.19	16.74	20.44
Phenantherene	0.00	0.00	0.00	0.02	0.44	1.29	2.35
Anthracene	0.00	0.00	0.00	0.03	0.37	0.81	1.39
Total PAHs	0.48	0.77	2.47	7.82	20.36	35.18	43.55



Current model predictions (full lines) of the main reaction products

Kinetic Modeling

- A **single-event** microkinetic model was generated using an automated reaction network generator, **RMG**
- Parameters requiring refinement are identified through **sensitivity analysis**
- **No fitting** of the parameters to the experimental data
- Individual reactions are subjected to an increased level of theoretical analysis
- Thermodynamics and kinetic data of sensitive species and reactions were calculated using quantum chemistry calculations at the **CBS-QB3** level using Gaussian 03

Conclusions

- Dedicated **GC×GC** setup combining **FID** and **TOF-MS**
- Implemented in an **on-line** analysis section of a bench scale set-up for (steam) **co-pyrolysis of CPD/C_2H_4**
- Detection of **PAHs** up to carbon number **C_{20}**
- Excellent agreement between **experiments** and **theory**

Acknowledgment

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